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Examination of hydrogen-bonding interactions between dissolved solutes and alkylbenzene solvents based on Abraham model correlations derived from measured enthalpies of solvation

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ABSTRACT

Enthalpies of solution at infinite dilution of 48 organic solutes in mesitylene and 81 organic solutes in *p*-xylene were measured using isothermal solution calorimeter. Enthalpies of solvation for 92 organic vapors and gaseous solutes in mesitylene and for 130 gaseous compounds in *p*-xylene were determined from the experimental and literature data. Abraham model correlations are determined from the experimental enthalpy of solvation data. The derived correlations describe the experimental gas-to-mesitylene and gas-to-*p*-xylene solvation enthalpies to within average standard deviations of 1.87 kJ mol^{-1} and 2.08 kJ mol^{-1}, respectively. Enthalpies of X—H···π (X—O, N, and C) hydrogen bond formation of proton donor solutes (alcohols, amines, chlorinated hydrocarbons etc.) with mesitylene and *p*-xylene were calculated based on the Abraham solvation equation. Obtained values are in good agreement with the results determined using conventional methods.

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1. Introduction

Enthalpies of solvation provide valuable insight regarding solute–solvent interactions and molecular complexation in fluid solution. Measured enthalpies of solvation, $\Delta_{solv}H^{\circ}$, can be used to test solution models and quantum chemical computations [1,2]. Experimental $\Delta_{solv}H^{\circ}$ can be utilized to extrapolate gas-to-liquid partition coefficients to system temperatures slightly higher and/or lower than the measurement temperature through standard thermodynamic relationships [3]. Solvation enthalpies have also been applied in chemical kinetic studies to model solvent effects on reaction rate parameters [4,5].

The present study continues our systematic combined experimental and theoretical examination of the transfer of nonelectrolyte solutes from the gas phase to organic solvents and to water. To date enthalpies of solvation have been reported for organic solutes dissolved in both dichloromethane and 1,4-dioxane [6], for amines dissolved in aliphatic alcohols and *vice versa* [7–9], for formamide and methylformamide derivatives dissolved in organic solvents [10], and for select ketones, nitriles and alkyl acetates dissolved in methanol and 1-octanol [11]. Results of the calorimetric measurements have provided thermodynamic functions pertaining to the formation of hydrogen-bonded complexes. Mathematical expressions have also been developed for calculating $\Delta_{solv}H^{\circ}$ values of organic vapors and gases dissolved in water [12] and 26 different organic solvents based on the Abraham solvation parameter model. The specific organic solvents studied include four alkanes (hexane [13], heptane [14], hexadecane [14] and cyclohexane [14]), two aromatic hydrocarbons (benzene [14] and toluene [15]), four chloroalkanes (chloroform [16], carbon tetrachloride [15], 1,2-dichloroethane [16], and dichloromethane [6]), three ethers (di-*n*-butyl ether [17], tetrahydrofuran [18] and 1,4-dioxane [6]), six primary alcohols (methanol [19], ethanol [19,20], propan-1-ol [18], butan-1-ol [19], octan-1-ol [12] and 2-methylpropan-1-ol [20]), two secondary alcohols (propan-2-ol [20] and butan-2-ol [20]), one tertiary alcohol (2-methylpropan-2-ol [21]), and six other organic solvents (acetonitrile [22], acetone [22], ethyl acetate [17], propylene carbonate [23], *N*,*N*-dimethylformamide [21], and dimethylsulfoxide [23]). The derived correlations back-calculate the observed $\Delta_{solv}H^{\circ}$ data to within an overall average standard deviation of less than ±3 kJ mol^{-1}.

The purpose of the present communication is to develop Abraham model correlations for enthalpies of solvation in mesitylene and *p*-xylene, and illustrate how the derived

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